

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY



(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

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Applicant's or agent's file reference TS 1249 PCT	FOR FURTHER ACTION See Form PCT/PEA/416	
International application No. PCT/EP2004/052379	International filing date (day/month/year) 30.09.2004	Priority date (day/month/year) 30.09.2003
International Patent Classification (IPC) or national classification and IPC C07C1/04, B01J23/75, B01J21/06		
Applicant SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.		
<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 5 sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input checked="" type="checkbox"/> sent to the applicant and to the International Bureau a total of 3 sheets, as follows:</p> <p><input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p>b. <input type="checkbox"/> (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>		
<p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the opinion</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI Certain documents cited</p> <p><input type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input type="checkbox"/> Box No. VIII Certain observations on the international application</p>		
Date of submission of the demand 07.07.2005	Date of completion of this report 09.11.2005	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Holzwarth, A Telephone No. +49 89 2399-7269 	

**INTERNATIONAL PRELIMINARY REPORT
ON PATENTABILITY**

International application No.
PCT/EP2004/052379

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.
- ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
- ☐ international search (under Rules 12.3 and 23.1(b))
 - ☐ publication of the international application (under Rule 12.4)
 - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)
2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report):*

Description, Pages

1-19 as originally filed

Claims, Numbers

1-14 received on 15.07.2005 with letter of 15.07.2005

- ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing
3. ☐ The amendments have resulted in the cancellation of:
- ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
 - ☐ any table(s) related to sequence listing (*specify*):
4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
- ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
 - ☐ any table(s) related to sequence listing (*specify*):

* If item 4 applies, some or all of these sheets may be marked "superseded."

**INTERNATIONAL PRELIMINARY REPORT
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Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	1-14
	No: Claims	1-6,9,10
Inventive step (IS)	Yes: Claims	7-8,11-14
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-14
	No: Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

Re Item V

**Reasoned statement with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement**

Reference is made to the following documents:

- D3: POTTIER, A. ET AL.: "Synthesis of brookite TiO₂ nanoparticles by thermolysis of TiCl₄ in strongly acidic aqueous media" JOURNAL OF MATERIALS CHEMISTRY, vol. 11, 2001, pages 1116-1121, XP002275120
- D5: WO 97/00231 A (SHELL INT RESEARCH ;SHELL CANADA LTD (CA)) 3 January 1997 (1997-01-03)

1. The present application does not meet the criteria of Article 33(1) PCT, because of the following reasons:

1.1 D3 (page 1116, paragraph introduction, lines 1-10) discloses a preparation process for titanium dioxide with high brookite content of more than 80 wt%. It has to be stressed, that the general teaching of D3 points to the selection of titania with a high brookite content. In D3 it is mentioned that the material is suitable as a catalyst carrier.

It is mentioned in the description (page 6, lines 23-28) of the present application that titania according to the invention can be prepared by the procedure disclosed in D3, so that the same materials must result.

The advantages of using brookite titania carriers in Co/TiO₂ Fischer-Tropsch catalysts, as they are shown in the present application, largely relate to the reduced formation of CoTiO₃. It is not credible that these advantages would be present for any type of catalyst containing titania carrier with a high brookite content.

As shaping is a standard operation in the preparation of catalyst carriers, no inventive step can be recognized for the subject matter of claim 1. The same is true for claim 9, which describes standard shaping techniques and claim 10, which describes standard techniques of metal salt deposition.

Therefore the subject-matter of at least claim 1, 9 and 10 does not involve an inventive step in view of D3 in the sense of Article 33(3) PCT.

1.2 Dependent claims 2-6 do not appear to contain any additional features which, in combination with the features of any claim to which they refer, meet the requirements of the

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(SEPARATE SHEET)**

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PCT with respect to novelty and/or inventive step, because said additional features are either disclosed in the prior art documents (see above) or are trivial or within the competence of a skilled person looking for alternative materials.

2. In the example section of the application it is shown that the choice of a high brookite content carrier as a support for cobalt yields a catalyst, which upon thermal and hydrothermal treatment show decreased formation of unwanted CoTiO_3 . Although no actual data are given in the application, it is credible that this is of advantage for Co/TiO_2 -Fischer-Tropsch catalysts. **D5** (claim 2, examples; closest prior art) discloses Co/TiO_2 Fischer-Tropsch catalysts. Claim 7 of the present application describes a catalyst comprising Group a VIII metal and a carrier according to claims 1-6 with a high brookite content. As group VIII metals can be in the largest sense be regarded as Fischer-Tropsch active metals, and neither **D3** (see above) nor **D5** disclose Group VIII catalysts using titania with a high brookite content (novelty) an inventive step can be recognized for the subject matter of claims 7 and dependant claims 11-14.

C L A I M S

1. Shaped catalyst carrier containing crystalline titania, wherein at least 50 wt% of the crystalline titania is present as brookite and wherein the carrier comprises between 40 and 100 wt% of crystalline titania based on the total weight of the carrier, preferably between 70 and 100 wt%, the shaped catalyst carrier not being a coated catalyst carrier.
2. The carrier of claim 1, wherein at least 50 wt% of the crystalline titania is present as brookite.
3. The carrier of claims 1-2, wherein at most 90 wt% of the crystalline titania is present as brookite, preferably at most 80 wt%.
4. The carrier of any of claims 1-3, wherein the crystalline titania is present as rutile in the range of from 0 to 50 wt%, preferably in the range of from 5 to 30 wt% and wherein the crystalline titania is present as anatase in the range of from 0 to 10 wt%, preferably in the range of from 0 to 5 wt%.
5. The carrier of any of claims 1-4, wherein the primary particle size of the brookite is in the range of from 10 to 100 nm, preferably of from 20 to 70 nm.
6. The carrier of anyone of claims 1-5, wherein also a binder is present, preferably silica, alumina or a combination of the two of them, and wherein the binder forms in the range of from 0 to 20 wt% of the carrier, preferably in the range of from 0 to 10 wt%.
7. Catalyst or catalyst precursor, comprising a Group VIII metal or a Group VIII metal compound and the carrier of claims 1-6 the Group VIII element preferably being Ru, Fe, Co or Ni, more preferably Co.

8. Catalyst or catalyst precursor according to claim 7, which furthermore comprises one or more metals or metal compounds of Group IIa, IIb, IVb, Vb, VIb, preferably manganese and zirconium oxide, or

which furthermore comprises one or more metals of Group VIIb and VIII, preferably rhenium, platinum and palladium:

9. Process for the preparation of a shaped catalyst carrier according to claims 1-6, by spray-drying, pressing, extruding or otherwise forcing a granular or powdered catalyst material into various shapes, preferably by extrusion.

10. Process for the preparation of a catalyst or a catalyst precursor according to anyone of claims 7-9, by impregnation or deposition precipitation of the shaped catalyst carrier according to anyone of claims 1-9 with a solution of one or more metal salts, followed by drying and calcination.

11. Process for the preparation of a catalyst or a catalyst precursor according to claim 7 or 8, comprising:

(a) mixing (1) titania in which at least 50 wt% of the crystalline titania is present as brookite, (2) a liquid, and (3) a Group VIII containing compound, which is at least partially insoluble in the amount of liquid used, to form a mixture,

(b) shaping and drying of the mixture thus-obtained, and

(c) calcination of the mixture thus-obtained.

12. Process according to claim 11, wherein the Group VIII containing compound is a metallic cobalt containing compound, a cobalt hydroxide containing compound or a cobalt oxide, preferably a $\text{Co}(\text{OH})_2$ or a Co_3O_4 containing compound, and wherein the cobalt containing compound further comprises a Group IVb and/or a Group VIIb compound, preferably a zirconium, manganese or rhenium compound.

13. An activated catalyst suitable for the production of hydrocarbons obtained by reduction with hydrogen at elevated temperature of a catalyst or a catalyst precursor according to claim 7 or 8.

14. Process for the preparation of hydrocarbons comprising contacting a mixture of carbon monoxide and hydrogen with a catalyst according to claim 13, optionally followed by hydroisomerisation/hydrocracking of the hydrocarbon product as obtained to produce middle distillate products.